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PATENT ABSTRACTS OF JAPAN

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(54) HARDCOAT FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To give superior abrasion resistance and weatherability to a film, and lessen deterioration caused by even providing an optical catalyst layer by laminating in turn a UV ray cutting layer and a hardcoat layer containing a silicon compound having a siloxane combination on one surface of a transparent base material film.

SOLUTION: A hardcoat film layer is manufactured by laminating by turns a UV ray cutting layer and a hardcoat layer containing a silicon compound having a siloxane combination on one surface of a transparent base material film. In this case, the UV ray cutting layer is preferable to be a layer consisting of one layer or two layer or more containing at least one kind selected from a UV ray diffuser and UV ray absorbent. The transparent base material film can be selected from a transparent plastic film, and as a concrete example thereof, there is a film of polyethylene, polypropylene or the like. Furthermore, given as a concrete example of the UV ray diffuser is powder obtained by minutely granulating titanium dioxide, zinc oxide, cerium oxide or the like.

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CLAIMS

[Claim(s)]
[Claim 1] The hard-coat film characterized by preparing the hard-coat layer containing the silicon compound which has an ultraviolet-rays shielding layer and siloxane combination in one field of a transparent base-material film one by one.
[Claim 2] The hard-coat film according to claim 1 which is the layer which consists of a monostromatic in which an ultraviolet-rays shielding layer contains at least one sort chosen from the ultraviolet-rays dispersion agent and the ultraviolet ray absorbent, or more than a bilayer.
[Claim 3] The hard-coat film according to claim 2 whose ultraviolet-rays shielding layer is a layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder.
[Claim 4] The hard-coat film according to claim 2 whose ultraviolet-rays shielding layer is a layer which contains an ultraviolet ray absorbent in an organic system binder.
[Claim 5] The hard-coat film according to claim 2 which is the two-layer structure to which an ultraviolet-rays shielding layer comes to carry out the laminating of the layer which contains an ultraviolet ray absorbent in an organic system binder, and the layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder from a base-material film side one by one.
[Claim 6] The hard-coat film according to claim 1 to 5 which comes to prepare a primer layer between an ultraviolet-rays shielding layer and a base-material film.
[Claim 7] The hard-coat film according to claim 1 to 6 whose hard-coat layer containing a silicon compound with siloxane combination is a layer which contains an inorganic silica system compound and/or a polyorganosiloxane system compound as a principal component.
[Claim 8] The hard-coat film according to claim 1 to 7 with which it comes to prepare an exfoliation sheet in the opposite side of the field in which the hard-coat layer of a transparent base-material film was prepared through a binder layer.
[Claim 9] The hard-coat film according to claim 1 to 8 used as an object for outside surface pasting of a windowpane or the plastics board for apertures.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention has the outstanding abrasion-proof nature, outstanding weatherability, etc. in more detail about a new hard-coat film, and relates to a hard-coat film suitable as objects for outside surface pasting, such as a windowpane and a plastics board for apertures, especially.
[0002]
[Description of the Prior Art] Conventionally, plastic film is used as a windowpane or an object for apertures for plastics board pasting for various purposes. For example, ultraviolet rays, infrared radiation, etc. are included in the sunlight which enters indoors from a windowpane in addition to the visible ray. It is also that it is known well that the ultraviolet rays included in sunlight will cause suntan, and the bad influence to a human body will be pointed out recently, and transformation of contents will arise owing to degradation of the packing material by ultraviolet rays. On the other hand, the indoor temperature rise by direct rays is caused also about the infrared radiation included by the sun, and there is a problem of reducing the air conditioning effect of summer. Therefore, in order to avoid such a situation that is not desirable, the ultraviolet-rays cover film and the infrared cover film are used as a windowpane or an object for apertures for plastics board pasting. Moreover, sticking an internal **** film on a windowpane or the plastics board for apertures is also often performed the that the interior of a room makes it hard to be visible from the exterior purpose. When a windowpane is furthermore damaged with calamities, such as an earthquake, in order to prevent that glass fragment disperses, the fragment scattering prevention film is used as an object for windowpane pasting. In addition, the aforementioned ultraviolet-rays cover film, the infrared cover film, and the internal **** film also have such a fragment scattering prevention effect. The hard-coat layer which these windowpanes and the plastics board pasting film for apertures (a window film may be called hereafter) carry out coating of an ionizing-radiation hardening type resin, for example, a polyester acrylate system, an epoxy acrylate system, an urethane acrylate system, the polyol acrylate system resin, etc. to the front face, and come to harden at it in order to usually give abrasion-proof nature etc. is prepared. By the way, in order to give weatherability to this hard-coat layer, it becomes the factor which decreases the abrasion-proof nature of a hard-coat side when an ultraviolet-rays dispersion agent is added, and when an ultraviolet ray absorbent is added on the other hand, ionizing-radiation hardening is barred or it becomes the factor which lowers abrasion-proof nature. Therefore, it was difficult to obtain the satisfactory ultraviolet-rays prevention to a base-material film with the conventional hard-coat film. Therefore, generally the window film is stuck on inside front faces, such as a windowpane. When it sticks on an outside front face, degradation by the ultraviolet rays of a hard-coat layer or a base-material film prepared in the film front face is intense, and a front face becomes dirty and this is because the life is remarkably short. By the way, since it was found out that semiconductors, such as a titanium dioxide, have a strong photocatalyst operation, development and utilization research of a photocatalyst have come to be done briskly in recent years. If this photocatalyst excites the semiconductor represented with a titanium

dioxide with the light of the energy more than the band gap Decomposition and removal of the various matter which an electron arises in a conduction band, and an electron hole is generated in a valence band, and applies such a photocatalyst operation using the electronic-electron hole pair which was rich in this energy, for example, poses a problem on the environmental pollution waste underwater one and in waste gas, deodorization, antifouling, antibacterial, sterilization, etc. are considered. Moreover, if the light which has the energy more than a band gap is irradiated as such a photocatalyst was described above, an electron generates to the conductor of a photocatalyst, an electron hole generates to a valence band, polarity is given by operation of this electron and/or an electron hole on a front face, and being hydrophilicity[super-]-ized is known. Therefore, using the super-hydrophilic property and antifouling performance of such a photocatalyst, a photocatalyst layer is prepared in the front face of a window film, and to stick this film on side-front front faces, such as a glass window, is tried recently. this attempt adhered to the film front face by irradiation of sunlight, and the repeat of a rainfall -- becoming dirty (organic substance) -- it is automatically made clean using the super-hydrophilic property and an antifouling performance, without cleaning -- making (self-cleaning) -- antifog [of a windowpane], rainy weather field-of-view reservation, etc. are aimed at However, in the conventional window film, since the hard-coat layer prepared in the front face made the subject the hardening resin which is the organic substance as described above, when a photocatalyst layer was prepared on this and a hard-coat layer deteriorated promptly by the photocatalyst operation, since a window film was **(ed) by direct ultraviolet rays, degradation of the base-material film itself also advanced quickly, and had problems, like a life is very short.

[0003]

[Problem(s) to be Solved by the Invention] While having abrasion-proof nature, weatherability, etc. which whose this invention is the basis of such a situation and were excellent, even if it prepares a photocatalyst layer in a front face, there is little degradation by it, and can be degradation also preparing the layer which has antibacterial, and it is made for the purpose of offering a hard-coat film suitable as objects for outside surface pasting, such as a windowpane and a plastics board for apertures, especially.

[0004]

[Means for Solving the Problem] The laminated film which prepared the ablation sheet in the opposite side through the binder layer by request finds out that the purpose may be suited, and this invention persons came to complete this invention based on this knowledge while preparing the hard-coat layer which consists of an ultraviolet-rays shielding layer and specific matter one by one in one field of a base-material film, as a result of repeating research wholeheartedly that the hard-coat film which has the aforementioned outstanding performance should be developed. That is, this invention offers the hard-coat film characterized by preparing the hard-coat layer containing the silicon compound which has an ultraviolet-rays shielding layer and siloxane combination in one field of (1) transparent base-material film one by one. Moreover, the hard-coat film given in ** (1) term which is the layer which consists of a monostromatic which, as for the desirable mode of this invention, contains at least one sort as which (2) ultraviolet-rays shielding layer was chosen from the ultraviolet-rays dispersion agent and the ultraviolet ray absorbent, or more than a bilayer, (3) The hard-coat film given in ** (2) term a given ultraviolet-rays shielding layer is a layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder, (4) The layer to which the hard-coat film given in ** (2) term a given ultraviolet-rays shielding layer is a layer which contains an ultraviolet ray absorbent in an organic system binder, and (5) ultraviolet-rays shielding layer contain an ultraviolet ray absorbent in an organic system binder from a base-material film side, The hard-coat film given in ** (2) term which is the two-layer structure which comes to carry out the laminating of the layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder one by one, (6) A hard-coat film ** (1) which comes to prepare a primer layer between an ultraviolet-rays shielding layer and a base-material film - given in (5) terms, (7) the hard-coat layer containing a silicon compound with siloxane combination A hard-coat film ** (1) which is the layer which contains an inorganic silica system compound and/or a polyorganosiloxane system compound as a principal component - given in (6) terms, (8) Hard-coat film given in ** (1) - (7) term with which it comes to prepare an ablation sheet in the opposite side of the

field in which the hard-coat layer of a transparent base-material film was prepared through a binder layer. (9) the hard-coat film given in ** (1) - (8) term used as an object for outside surface pasting of a windowpane or the plastics board for apertures -- come out

[0005]

[Embodiments of the Invention] As a transparent base-material film used for the hard-coat film of this invention, there is especially no limit, according to a situation, can be chosen suitably and can be used out of various transparent plastic film. As this transparent plastic film, for example Polyethylene, polypropylene, Polyolefine system resins, such as the poly 4-methyl pentene -1 and a polybutene -1, Polyester system resins, such as a polyethylene terephthalate and polyethylenenaphthalate, A polycarbonate system resin, a polyvinyl chloride system resin, a polyphenylene sulfide system resin, A polyether ape phon system resin, a polyethylene sulfide system resin, The films which consist of cellulose system resins, such as a polyphenylene-ether system resin, a styrene resin, an acrylic resin, a polyamide system resin, a polyimide system resin, and a cellulose acetate, etc., or these laminated films are mentioned. Although what is necessary is for there to be especially no limit as thickness of this transparent base-material film, and just to select suitably according to the purpose of use, 5-200 micrometers is usually the range of 10-100 micrometers preferably. Moreover, this transparent base-material film may be colored or deposited by the request, and may contain the ultraviolet ray absorbent. Furthermore, surface treatment can be performed to one side or both sides by the oxidation style, the irregularity-ized method, etc. a request in order to raise adhesion with the layer prepared in the front face. As the above-mentioned oxidation style, corona discharge processing, a chromate treatment (wet), a flame treatment, hot blast processing, ozone, UV irradiation processing, etc. are mentioned, for example, and the sandblasting method, a solvent approach, etc. are mentioned as an irregularity-ized method, for example. Although these surface treatment methods are suitably chosen according to the kind of base-material film, generally a corona discharge approach is preferably used from fields, such as an effect and operability. In the hard-coat film of this invention, an ultraviolet-rays shielding layer and a hard-coat layer are prepared in one field of the aforementioned transparent base-material film one by one. The above-mentioned ultraviolet-rays shielding layer is a layer which contains at least one sort chosen from the ultraviolet-rays dispersion agent and the ultraviolet ray absorbent as an ultraviolet-rays shielding material, by containing these ultraviolet-rays shielding materials, ultraviolet rays are intercepted effectively and degradation by the ultraviolet rays of a base-material film is suppressed. Here, an ultraviolet-rays dispersion agent is a material which brings about an ultraviolet-rays screening effect by scattering ultraviolet rays, and inorganic system material, such as metallic-oxide powder, is mainly used. As an example of this ultraviolet-rays dispersion agent, the fine particles which atomized the titanium dioxide, the zinc oxide, the cerium oxide, etc. or the hybrid inorganic fine particles which comes to process a titanium-dioxide particle with an iron oxide composite-ization, the hybrid inorganic fine particles which come to coat the front face of a cerium-oxide particle with an amorphous nature silica are mentioned. An ultraviolet-rays scattering effect receives influence in a particle diameter greatly, in this invention, 3 micrometers or less are desirable and the mean particle diameter of the aforementioned ultraviolet-rays dispersion agent has the especially desirable range which is 1nm - 1.5 micrometers. On the other hand, ultraviolet rays with a high energy are absorbed and it converts into harmless energy, and by re-radiating, an ultraviolet ray absorbent can bring about an ultraviolet-rays screening effect, and can raise the lightfastness and weatherability of plastics, and, generally can be divided roughly into a SARISHI rate system, a benzophenone system, a benzotriazol system, a substitution acrylonitrile system, and others. As an example of a SARISHI rate system ultraviolet ray absorbent, a phenyl SARISHI rate, p-octyl phenyl SARISHI rate, a p-t-buthylphenyl SARISHI rate, etc. are mentioned. as an example of a benzophenone system ultraviolet ray absorbent 2 and 2'-dihydroxy-4-methoxybenzophenone, 2, and 2'-dihydroxy -4, a 4'-dimethoxy benzophenone, A 2, 2', 4, and 4'-tetrapod hydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone, 2, 4-dihydroxy benzophenone, 2-hydroxy-4-octoxybenzophenone, etc. are mentioned. moreover, as an example of a benzotriazol system ultraviolet ray absorbent A 2-(2'-hydroxy-3' and 5'-G tert-buthylphenyl)-5-chloro benzotriazol, A 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chloro benzotriazol, A 2-(2'-hydroxy-3'-tert-amyl-5'-isobutyl

phenyl)-5-chloro benzotriazol, A 2-(2'-hydroxy-3'-isobutyl-5'-methylphenyl)-5-chloro benzotriazol, A 2-(2'-hydroxy-3'-isobutyl-5'-propyl phenyl)-5-chloro benzotriazol, 2-(2'-hydroxy-3' and 5'-G tert-buthylphenyl) benzotriazol, 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, 2-[2'-hydroxy-5'-(1, 1, 3, and 3-tetramethyl) phenyl] benzotriazol etc. is mentioned. as an example of a substitution acrylonitrile system ultraviolet ray absorbent The 2-cyano -3, 3-diphenyl ethyl acrylate, the 2-cyano -3, 3-diphenyl acrylic-acid 2-ethylhexyl, etc. are mentioned. Furthermore, in addition to this as an ultraviolet ray absorbent, resorcinol monochrome benzoate, 2, 4-G t-buthylphenyl -3, 5-G t-butyl-4-hydroxy benzoate, an N-(2-ethyl phenyl)-N'-(2-ethoxy-5-t-buthylphenyl) oxalic acid diamide, etc. are mentioned, for example.

[0006] In addition, you may use by request what raises the lightfastness and weatherability like a hindered amine system as a light stabilizer combining the aforementioned ultraviolet ray absorbent. In this invention, these ultraviolet-rays shielding materials may be used independently, and may be used combining two or more sorts. Moreover, although there is especially no limit as a content of this ultraviolet-rays shielding material in an ultraviolet-rays shielding layer and it is suitably selected according to the kind of ultraviolet-rays shielding material, the kind of base-material film, etc., it is usually 0.05 - 5% of the weight of a range preferably 0.01 to 10% of the weight. In addition, when an ultraviolet-rays shielding material is an ultraviolet-rays dispersion agent, the content has 0.1 - 10% of the weight of a desirable range, and 1 - 5% of the weight of the range is especially suitable for it. On the other hand, when ultraviolet-rays shielding materials are an ultraviolet ray absorbent and a light stabilizer, the content has 0.01 - 10% of the weight of a desirable range, and 0.05 - 5% of the weight of its range is especially desirable.

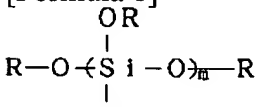
[0007] The ultraviolet-rays shielding layer in the hard-coat film of this invention may be a layer which consists of a suitable binder and the aforementioned ultraviolet-rays shielding material contained in it, may be a monolayer, and may have more than the bilayer, for example, the laminated structure of 2-10 layers, if needed. Although there is especially no limit as the above-mentioned binder and both inorganic and an organic substance can be used, when an ultraviolet-rays shielding material is the ultraviolet-rays dispersion agent of an inorganic system particle, a silicon system binder is desirable, and when it is an ultraviolet ray absorbent on the other hand, an organic system binder is desirable. The thing of the two-layer structure which comes to carry out the laminating of the layer which contains an ultraviolet ray absorbent in an organic system binder, and the layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder from layer [which contains an inorganic system ultraviolet-rays dispersion agent, for example in (1) silicon system binder], layer [which contains an ultraviolet ray absorbent in (2) organic system binder], and (3) base-material film side one by one as composition of this ultraviolet-rays shielding layer is suitable. As the above-mentioned silicon system binder, there is especially no limit, for example, it can mention an inorganic silica system (the poly silicic acid is also included), polyorganosiloxane systems, or these mixed stocks. These can be conventionally manufactured by well-known various methods.

For example, a general formula [1]

R1nSi(OR2)4-n -- [1]

R1 in [formula is a non-adding water resolvability machine, an alkyl group, a substitution alkyl group, alkenyl machines (substituent : a halogen atom, an epoxy group, a (meth)acryloyloxy machine, etc.), an aryl group or an aralkyl machine, and R2 are low-grade alkyl groups, and n is the integer of 0, or 1-3. When there are two or more R1 and OR2, respectively, even if two or more R1 is the same, it may differ, and even if two or more OR2 is the same, it may differ.] The method of appearing, understanding the alkoxysilane compound expressed by the portion or full adding water, and carrying out a polycondensation using organic acids, such as inorganic acids, such as a hydrochloric acid and a sulfuric acid, oxalic acid, and an acetic acid, is used preferably. In this case, if n understands by full adding water, the compound, i.e., the tetrapod alkoxysilane, of 0, the binder of an inorganic silica system will be obtained, and if partial hydrolysis is carried out, a polyorganosiloxane system binder or the mixed-stock binder of an inorganic silica system and a polyorganosiloxane system will be obtained. On the other hand, since n has a non-adding water resolvability machine with the compound of 1-3, a

polyorganosiloxane system binder is obtained by the portion or full hydrolysis. Under the present circumstances, in order to hydrolyze uniformly, you may use a suitable organic solvent.
[0008] As an example of an alkoxysilane compound expressed with the aforementioned general formula [1] A tetramethoxy silane, a tetrapod ethoxy silane, tetrapod-n-propoxysilane, Tetrapod isopropoxysilane, tetrapod-n-butoxysilane, tetrapod iso butoxysilane, Tetrapod-sec-butoxysilane, tetrapod-tert-butoxysilane, Methyl trimetoxysilane, methyl triethoxysilane, MECHIRUTORI propoxysilane, A methyl triisopropoxy silane, ethyl trimethoxysilane, ethyltriethoxysilane, Propyl triethoxysilane, butyltrimethoxysilane, phenyl trimethoxysilane, Phenyl triethoxysilane, gamma-glycidoxypropyltrimetoxysilane, gamma-acryloyloxypropyl trimethoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, Dimethyl dimethoxysilane, methylphenyl dimethoxysilane, vinyltrimetoxysilane, vinyltriethoxysilane, divinyl dimethoxysilane, divinyl diethoxysilane, a TORIBI nil methoxy silane, a TORIBI nil ethoxy silane, etc. are mentioned. These may be used independently and may be used combining two or more sorts. Moreover, if required in this case, suitable amount addition of an aluminium compound, for example, an aluminum chloride, the thoria RUKOKI sial minium, etc. can be carried out. Furthermore, a meta-sodium silicate, an orthochromatic sodium silicate, or water glass (sodium-silicate mixture) can be used for the silicon compound of a raw material, metallic compounds, such as acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, or a magnesium chloride, and a calcium sulfate, can be made to be able to act as an option, and the method of carrying out hydrolysis processing can be used. Although it is easy to carry out the polymerization of this thing by this hydrolysis processing although the silicic acid of isolation generates, and it changes with kinds of raw material, it is the mixture of the thing of the shape of the shape of a chain, annular, and a mesh. The poly silicic acid obtained from water glass is a general formula [2].
[Formula 1]



… [2]

(-- m in a formula shows polymerization degree and R is metals, such as hydrogen, silicon or magnesium, and aluminum, the thing of the chain structure expressed with) -- a subject -- ** Thus, a perfect inorganic silica system binder is obtained. In addition, silica gel (SiOX-nH2O) can also be used as an inorganic silica system binder. This ultraviolet-rays shielding layer is not required for a hard-coat performance by force, and a polyorganosiloxane system binder or the mixed-stock binder of an inorganic silica system and a polyorganosiloxane system is more suitable for it than a perfect inorganic silica system binder from the point of adhesion rather. On the other hand, as an organic system binder, there is especially no limit and a well-known thing, for example, an acrylic resin, a polyester system resin, a polyurethane system resin, a butyral system resin, etc. can mention the hardened material of an ionizing-radiation hardening type resin etc. further conventionally. Here, an ionizing-radiation hardening type resin is a resin hardened by irradiation of ultraviolet rays, an electron ray, etc., and the ultraviolet-rays hardening type resin currently conventionally used abundantly also especially in it at formation of the hard-coat layer of an indoor-type window film is suitable for it. As this ultraviolet-rays hardening type resin, an ultraviolet-rays hardening type polyester acrylate resin, an ultraviolet-rays hardening type epoxy acrylate resin, an ultraviolet-rays hardening type urethane acrylate resin, etc. can be mentioned, for example. Polyfunctional monomer, such as various single organic-functions monomers and ester of polyhydric alcohol and an acrylic acid (meta), can be added to this ultraviolet-rays hardening type resin if needed, and a photopolymerization initiator, for example, acetophenones, benzophenones, benzoins, and phenyl ketones are usually added and used for it.
[0009] The ultraviolet-rays shielding layer in this invention can be formed by preparing the aforementioned binder and the coating liquid containing an ultraviolet-rays shielding material, carrying out coating on a base-material film using a well-known method, for example, the bar coat method, the knife coat method, the roll coat method, the blade coat method, the die coat method, the gravure coat

method, etc. conventionally, irradiating heating or ionizing radiation and stiffening it. The range of 0.1-20 micrometers of thickness of this ultraviolet-rays shielding layer is usually 0.5-10 micrometers preferably. In this invention, in order to raise the adhesion of this ultraviolet-rays shielding layer and a base-material film, a primer layer can be prepared between an ultraviolet-rays shielding layer and a base-material film by request. If this primer layer is prepared when an ultraviolet-rays shielding layer is the composition of the above (1), i.e., the layer which contains an inorganic system ultraviolet-rays dispersion agent in a silicon system binder, it is especially effective. Although there is especially no limit as this primer and primers, such as a well-known thing, for example, acrylic, a polyester system, a polyurethane system, a silicone system, and a rubber system, can be used conventionally, points, such as endurance and adhesion, to acrylic and a polyester system primer are suitable. This primer can be made to contain an ultraviolet ray absorbent and a light stabilizer as occasion demands. From points, such as homogeneous application nature and adhesion, this primer layer thickness has the desirable range of 0.1-10 micrometers, and the range which is 0.5-5 micrometers is especially suitable for it. Moreover, the silver system inorganic antimicrobial agent which made the phosphoric-acid zirconium the support as an antimicrobial agent, The silver system inorganic antimicrobial agent which made the zeolite the support, the silver system inorganic antimicrobial agent which made calcium phosphate the support, Silver system inorganic antimicrobial agents, such as a silver system inorganic antimicrobial agent which made silica gel the support, the amino acid system organic antimicrobial agent which comes to blend an amino acid compound, What is necessary is just to carry out suitable amount combination into a resin constituent according to the kind of antimicrobial agent which various antimicrobial agents, such as a nitrogen content sulfur system organic antimicrobial agent which comes to blend a nitrogen content sulfur system compound, are used, and is used, antibacterial [which is needed], its holding time, etc. In the hard-coat film of this invention, a hard-coat layer is prepared on the ultraviolet-rays shielding layer formed by doing in this way. This hard-coat layer is a layer containing the silicon compound which has siloxane combination, for example, can mention preferably the layer which makes a principal component an inorganic silica system compound (the poly silicic acid is also included) and/or a polyorganosiloxane system compound. This inorganic silica system compound and a polyorganosiloxane system compound can be similarly manufactured by the method explained in the aforementioned silica system binder. In this hard-coat layer, it is the range in which required adhesion is maintained from importance being attached to a hard-coat performance, and the layer which contains many inorganic silica system compounds as much as possible is suitable. Moreover, this hard-coat layer can be made to contain the aforementioned inorganic system ultraviolet-rays dispersion agent etc. by request in the range by which abrasion-proof nature is not spoiled. This hard-coat layer can be formed by carrying out coating of the hard-coat material content coating liquid, heating it, and stiffening it on an ultraviolet-rays shielding layer, using a well-known method, for example, the bar coat method, the knife coat method, the roll coat method, the blade coat method, the die coat method, the gravure coat method, etc. Moreover, when forming the hard-coat layer which consists of an inorganic silica system compound, physical gaseous-phase vacuum depositions (PVD), such as a vacuum deposition method, SUPPATA Ling's method, and the ion plating method, can also be adopted.

[0010] Thus, the range of 0.05-30 micrometers of formed hard-coat layer thickness is usually 0.05-20 micrometers preferably. In the hard-coat film of this invention, an ablation sheet can be prepared in the near opposite side where it did in this way by request, and the ultraviolet-rays shielding layer and the hard-coat layer were prepared on the base-material film through a binder layer. Although there is especially no limit as a binder which constitutes the above-mentioned binder layer, and it can choose suitably and can use according to a situation out of well-known various binders conventionally, acrylic, an urethane system, and a silicone system binder are suitable from points, such as weatherability. The range of 5-100 micrometers of this binder layer thickness is usually 10-60 micrometers preferably. Moreover, as an ablation sheet prepared on this binder layer, what made removers, such as silicone resin, with ** paper and various plastic film, such as glassine, coat paper, and lamination paper, is mentioned, for example. Although there is especially no limit about the thickness of this ablation sheet, it is usually about 20-150 micrometers. In addition, the above-mentioned binder layer can be made to

contain an ultraviolet ray absorbent and a light stabilizer if needed. Especially the hard-coat film of this invention is suitably used as objects for outside surface pasting, such as a windowpane and a plastics board for apertures. When using it, an ablation sheet is removed, and as a binder stratification plane touches an object, it should just stick on it. Moreover, if required, it can print in arbitrary layers other than the hard-coat layer of the hard-coat film of this invention.

[0011]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, the physical properties of the hard-coat film produced in each example were searched for according to the following point. (1) Based on the pencil degree of hardness JIS K 5400, it measured by the hand or ****.

(2) Using the weatherproof weatherometer [the product made from SUGA Examination Machine, and a WEL-SUN-DC type], the accelerated weathering test of 1000 hours was carried out, visual observation of the appearance was carried out, and it evaluated in accordance with the criterion shown below.

O those with :-degradation-less x:degradation (3) -- -proof -- the hard-coat layer front face was rubbed by abrasion nature steel wool **0000, visual observation of the appearance was carried out, and it evaluated in accordance with the criterion shown below

O : -- x: to which a blemish is not attached -- MRSA fungus liquid (104 pieces/(ml)) was inoculated on (4) antibacterial film to which a blemish is attached (10microl/cm2), the bacillus was flushed after 3-hour neglect by 23 degrees C and 65%RH, and the number of micro organisms was measured in the culture medium for the number measurement of bacilli

(5) Visual observation of the dirt 500 hours after an antifouling-property outdoor exposure was carried out, and it evaluated in accordance with the following criterion.

O :-dirt-less x : write it as a PET film below polyethylene-terephthalate film [with a thickness of 50 micrometers as an example 1 base-material film with dirt.] by Toyobo Co., Ltd. "4100." It used, and after carrying out coating of the coating agent which consists of cerium-oxide powder [product [made from NIPPON MUKI Chemical industry] "auction guard S3018-02" and 1 micrometer of mean particle diameters] 2 % of the weight which is an ultraviolet-rays dispersion agent, and silicon system binder [COL Coat 98 "N-103X"] % of the weight to this one side by my YABA so that dryness thickness may be set to 2 micrometers, it was dried for 1 minute at 100 degrees C, and the ultraviolet-rays shielding layer was prepared in it. Subsequently, after carrying out coating of the coating agent [Product made from **** "GO-100SX"] which contains an inorganic silica system compound in this coat side by my YABA so that dryness thickness may be set to 3 micrometers, it was made to dry for 2 minutes at 100 degrees C, and the hard-coat layer was prepared. The physical properties of this hard-coat film are shown in the 1st table.

As an example 2 base-material film. "Lumiler Q37**25" by PET film [Toray Industries, Inc. [with a thickness of 25 micrometers] After performing corona discharge processing to both sides using ultraviolet ray absorbent content], on the one side The coating agent [the product "SERASUTATTSU 27" made from Parka Processing] which an inorganic silica system binder is made [coating agent] into a principal component, and comes to carry out little distribution of the cerium-oxide powder which is an ultraviolet-rays dispersion agent After carrying out coating by my YABA so that dryness thickness may be set to 3 micrometers, it was made to dry for 2 minutes at 120 degrees C, and the ultraviolet-rays shielding layer was prepared. Subsequently, after carrying out coating of the coating agent ["ORGANO silica-sol CX-SZ" By NIPPON SHOKUBAI] containing a polyorganosiloxane compound to this coat side by my YABA so that dryness thickness may be set to 5 micrometers, it was dried for 2 minutes at 120 degrees C, and the hard-coat layer was prepared in it. The physical properties of this hard-coat film are shown in the 1st table.

As an example 3 base-material film. A polyether ape phon film ["TALPA-1000" by Mitsui Toatsu Chemicals, Inc.] with a thickness of 25 micrometers is used. The product made from titanium-dioxide powder [Ishihara Techno which is an ultraviolet-rays dispersion agent at the one side after performing corona discharge processing to both sides, After carrying out coating of the coating agent which consists of 20nm [of mean particle diameters]] 2 % of the weight, and silicon system binder [COL Coat 98 "N-

103X"] % of the weight by my YABA so that dryness thickness may be set to 2 micrometers, it was made to dry for 1 minute at 100 degrees C, and the ultraviolet-rays shielding layer was prepared. Subsequently, after carrying out coating of the coating agent ["FURESSERA" by Matsushita Electric Works, Ltd.] which contains an inorganic silica system compound in this coat side by my YABA so that dryness thickness may be set to 3 micrometers, it was made to dry for 5 minutes at 100 degrees C, and the hard-coat layer was prepared. The physical properties of this hard-coat film are shown in the 1st table.

As an example 4 base-material film. After carrying out coating of the coating agent which becomes the one side from the tinuvin 1130 [Tiba Speciality Chemicals 0.1] % of the weight which is an ultraviolet ray absorbent, and organic urethane system binder [99.9 "super FREX 410" by Dai-Ichi Kogyo Seiyaku Co., Ltd.] % of the weight using a PET film ["4100" by Toyobo Co., Ltd.] with a thickness of 50 micrometers by my YABA so that dryness thickness may be set to 2 micrometers, it was dried for 2 minutes at 120 degrees C, and the ultraviolet-rays shielding layer was prepared. Subsequently, after carrying out coating of the coating agent [the product "SERASUTATTSU 17" made from Parka Processing] containing an inorganic silica system compound to this coat side by my YABA so that dryness thickness may be set to 3 micrometers, it was dried for 2 minutes at 120 degrees C, and the hard-coat layer was made to form in it. The physical properties of this hard-coat film are shown in the 1st table.

As an example 5 base-material film. After carrying out coating of the coating agent which becomes the one side from the tinuvin 1130 [Tiba Speciality Chemicals 0.1] % of the weight which is an ultraviolet ray absorbent, and organic urethane system binder [99.9 "super FREX 410" by Dai-Ichi Kogyo Seiyaku Co., Ltd.] % of the weight using a PET film ["4100" by Toyobo Co., Ltd.] with a thickness of 50 micrometers by my YABA so that dryness thickness may be set to 2 micrometers, it was dried for 2 minutes at 120 degrees C, and the ultraviolet-rays shielding layer was prepared. Subsequently, this coat side was made to carry out vacuum deposition of the silica gel (SiOX-nH2O) on condition that temperature [of 1000 degrees C], and pressure 5x10-3Torr, and the hard-coat layer which consists of a silicon oxide film with a thickness of 0.1 micrometers was made to form in it. Next, after carrying out coating of the toluene solution containing 97 % of the weight of butyl acrylates, and 3 % of the weight [of acrylic acids] 40 % of the weight of copolymers and 0.5 % of the weight of aluminum chelates to the opposite side of this PET film in a comma coating machine, it dried to it for 2 minutes at 100 degrees C, and the binder layer with a thickness of 20 micrometers was formed in it. Furthermore, lamination and the hard-coat adhesion film were produced for the ablation film ["SP-PET3811" by LINTEC Corp.] with a thickness of 38 micrometers. The physical properties of this hard-coat film are shown in the 1st table.

As an example 6 base-material film. A PET film ["lumiler **50" by Toray Industries, Inc.] with a thickness of 50 micrometers is used. After carrying out corona discharge processing of these both sides, on the one side Tinuvin 1130 [made in Tiba Speciality Chemicals] which is an ultraviolet ray absorbent 2 % of the weight, IRUGA cure [Tiba Speciality Chemicals 4] % of the weight which is a photopolymerization initiator, and ultraviolet-rays hardening type polyfunctional acrylate system binder [Toagosei Make "ARONIKKUSU M305"] After carrying out coating of the coating agent which consists of 94 % of the weight by my YABA so that the thickness after hardening may be set to 1 micrometer, the ultraviolet rays of 200 mJ/cm2 are irradiated, and were stiffened, and the 1st ultraviolet-rays shielding layer was prepared. Furthermore, on this, after carrying out coating of the coating agent which consists of cerium-oxide powder [product [made from NIPPON MUKI Chemical industry] "auction guard S3018-02" and 1 micrometer of mean particle diameters] 2 % of the weight which is an ultraviolet-rays dispersion agent, and silicon system binder [COL Coat 98 "N-103X"] % of the weight by my YABA so that dryness thickness may be set to 2 micrometers, it was made to dry for 1 minute at 100 degrees C, and the 2nd ultraviolet-rays shielding layer was prepared. Subsequently, after carrying out coating of the coating agent [Product made from **** "GO-100SX"] which contains an inorganic silica system compound in this coat side by my YABA so that dryness thickness may be set to 3 micrometers, it was made to dry for 2 minutes at 100 degrees C, and the hard-coat layer was prepared.

Next, after carrying out coating of the urethane system binder to the opposite side of this PET film in a comma coating machine, it dried to it for 3 minutes at 140 degrees C, and the binder layer with a thickness of 50 micrometers was formed in it. Furthermore, lamination and the hard-coat adhesion film were produced for the ablation film ["SP-PET3811" by LINTEC Corp.] with a thickness of 38 micrometers. In addition, the above-mentioned urethane system binder adds cross-linking-agent [product [made from Dainippon Ink Chemistry] "Chris Bon NX" and 75 % of the weight of concentration] 3 % of the weight to polyurethane elastomer [product [made from Dainippon Ink Chemistry] "Chris Bon 5150S" and 50 % of the weight of concentration] 97% of the weight. The physical properties of this hard-coat film are shown in the 1st table.

After carrying out coating of the polyester system primer ["Pori Ester WR-901" by the Nippon Synthetic Chemical Industry Co., Ltd.] to the one side after carrying out corona discharge processing of these both sides, using a PET film ["lumiler **50" by Toray Industries, Inc.] with a thickness of 50 micrometers as an example 7 base-material film by my YABA so that dryness thickness may be set to 1 micrometer, it was heated on it for 2 minutes at 100 degrees C, and the primer layer was prepared in it. On this primer layer, after carrying out coating of the coating agent which consists of cerium-oxide powder [product [made from NIPPON MUKI Chemical industry] "auction guard S3018-02" and 1 micrometer of mean particle diameters] 2 % of the weight which is an ultraviolet-rays dispersion agent, and silicon system binder [COL Coat 98 "N-103X"] % of the weight by my YABA so that dryness thickness may be set to 2 micrometers, it was made to dry for 1 minute at 100 degrees C, and the ultraviolet-rays shielding layer was prepared. Subsequently, after carrying out coating of the coating agent [Product made from **** "GO-100SX"] which contains an inorganic silica system compound in this coat side by my YABA so that dryness thickness may be set to 3 micrometers, it was made to dry for 2 minutes at 100 degrees C, and the hard-coat layer was prepared. Next, to the opposite side of this PET film, like the example 5, content] was prepared for with a thickness of 20 micrometers binder layer [, however ultraviolet ray absorbent "SUMISOBU 90" (Sumitomo Chemical Co., Ltd. make) 2 % of the weight, and lamination and the hard-coat adhesion film were further produced for the ablation film. The physical properties of this hard-coat film are shown in the 1st table.

On the hard-coat layer of example 8 example 2, it is a complex-ion support phosphoric-acid zirconium system antimicrobial agent further to [Byron 20SS and Toyobo Co., Ltd. make] made of polyester system resin 99.5 % of the weight [NOBARON AG300, the product made from Toagosei Chemistry, and 0.5 micrometers of mean particle diameters]. Using the partially aromatic solvent of toluene and a methyl ethyl ketone, coating of what was added 0.5% of the weight was carried out so that the thickness after dryness might be set to 0.2 micrometers in a gravure coating machine, and dryness processing was carried out for 30 seconds at 100 degrees C. The physical properties of this hard-coat film are shown in the 1st table.

On the hard-coat layer of example 9 example 2, further, coating of the product made from Ishihara Techno and titanium oxide ST-K03 was carried out so that the thickness after dryness might be set to 0.5 micrometers in a gravure coating machine, and dryness processing was carried out for 20 minutes at 140 degrees C. The physical properties of this hard-coat film are shown in the 1st table.

In example of comparison 1 example 1, the hard-coat film was produced like the example 1 except having not used the cerium-oxide powder which is an ultraviolet-rays dispersion agent. The physical properties are shown in the 1st table.

As an example of comparison 2 base-material film. A PET film ["4100" by Toyobo Co., Ltd.] with a thickness of 50 micrometers is used. The product made from cerium-oxide powder [NIPPON MUKI Chemical industry which is an ultraviolet-rays dispersion agent at the one side "auction guard S3018-02", After carrying out coating of the coating agent which consists of 1 micrometer [of mean particle diameters]] 2 % of the weight, and binder [Product made from **** "GO-100SX"] 98 % of the weight containing an inorganic silica system compound by my YABA so that dryness thickness may be set to 2 micrometers, it was made to dry for 1 minute at 100 degrees C. The physical properties of this hard-coat film are shown in the 1st table.

[0012]

[Table 1]
第1表

	鉛筆硬度	耐候性	耐擦傷性	抗菌性	防汚性
実施例1	2H	○	○	−	−
実施例2	4H	○	○	−	−
実施例3	2H	○	○	−	−
実施例4	2H	○	○	−	−
実施例5	F	○	○	−	−
実施例6	2H	○	○	−	−
実施例7	2H	○	○	−	−
実施例8	2H	○	○	<10	−
実施例9	3H	○	○	−	○
比較例1	2H	×	○	−	−
比較例2	B	○	×	−	−

[0013]
[Effect of the Invention] Even if the hard-coat film of this invention has the outstanding abrasion-proof nature, outstanding weatherability, etc. and moreover prepares a photocatalyst layer, it has little degradation by it, is possible also for preparing the layer which has antibacterial, and especially suitable as objects for outside surface pasting, such as a windowpane and a plastics board for apertures.

[Translation done.]